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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

ASSISTANT COMMISSIONER FOR PATENTS

Washington, D.C. 20231

Attorney's Docket Number: 01222.0034-01000

Prior Application:

Art Unit: 1755

Examiner: D. Brunsman

SIR: This is a request for filing a

Continuation  Divisional Application under 37 C.F.R. § 1.53(b) of pending prior application Serial No. 08/544,212 filed October 17, 1995 of David A. RUSSO, Ryan R. DIRKX and Glenn P. FLORCZAK for COATING COMPOSITION FOR GLASS

[Title of Invention]

1.  Enclosed is a complete copy of the prior application including the oath or Declaration and drawings, if any, as originally filed. I hereby verify that the attached papers are a true copy of prior application Serial No. 08/544,212 as originally filed on October 17, 1995.
2.  Enclosed is a substitute specification under 37 C.F.R. § 1.125.
3.  Cancel Claims \_\_\_\_\_.
4.  A Preliminary Amendment is enclosed.
5.  The filing fee is calculated on the basis of the claims existing in the prior application as amended at 3 and 4 above.

For	: Number Filed	: Number Extra	: Rate	: Basic Fee	\$760.00
Total	:	:	:	:	
Claims	: 32 -20	: 12	: x\$ 18.00=	\$ 216.00	
Independent	:	:	:	:	
Claims	: 5 -3=	: 2	: x\$ 78.00=	\$ 156.00	

Multiple Dependent Claim(s) (if applicable)	: +\$260.00=:
	Total = : \$
Reduction by ½ for	:
filing by small entity	:
TOTAL FILING FEE	= : \$ 1,132.00

6.  A check in the amount of \$ 1,132.00 to cover the filing fee is enclosed.
7.  The Commissioner is hereby authorized to charge any fees which may be required including fees due under 37 C.F.R. § 1.16 and any other fees due under 37 C.F.R. § 1.17, or credit any overpayment during the pendency of this application to Deposit Account No. 06-0916.
8.  Amend the specification by inserting before the first line, the sentence:  
--This is a  continuation  division of application Serial No. 08/544,212, filed October 17, 1995 which is a RE of 08/104,125, December 13, 1993, Patent No. 5,401,305, all of which are incorporated herein by reference.--
9.  New formal drawings are enclosed.
10.  The prior application is assigned of record to: ELF ATOCHEM NORTH AMERICA, INC.
11.  Priority of application Serial No. \_\_\_\_\_, filed on \_\_\_\_\_ in \_\_\_\_\_ (country) is claimed under 35 U.S.C. § 119. A certified copy  
 is enclosed or  is on file in the prior application.
12.  A verified statement claiming small entity status  
 is enclosed or  is on file in the prior application.
13.  The power of attorney in the prior application is to at least one of the following: FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, L.L.P., Douglas B. Henderson, Reg. No. 20,291; Ford F. Farabow, Jr., Reg. No. 20,630; Arthur S. Garrett, Reg. No. 20,338; Donald R. Dunner, Reg. No. 19,073; Brian G. Brunsvold, Reg. No. 22,593; Tipton D. Jennings, IV, Reg. No. 20,645; Jerry D. Voight, Reg. No. 23,020; Laurence R. Hefter, Reg. No. 20,827; Kenneth E. Payne, Reg. No. 23,098; Herbert H. Mintz, Reg. No. 26,691; C. Larry O'Rourke, Reg. No. 26,014; Albert J. Santorelli, Reg. No. 22,610; Michael C. Elmer, Reg. No. 25,857; Richard H. Smith, Reg. No. 20,609; Stephen L. Peterson, Reg. No. 26,325; John M. Romary, Reg. No. 26,331; Bruce C. Zotter, Reg. No. 27,680; Dennis P. O'Reilley, Reg. No. 27,932; Allen M. Sokal, Reg. No. 26,695; Robert D. Bajefsky, Reg.

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14.  The power appears in the original declaration of the prior application.
15.  Since the power does not appear in the original declaration, a copy of the power in the prior application is enclosed.
16.  Please address all correspondence to FINNEGAN, HENDERSON, FARABOW, GARRETT and DUNNER, L.L.P., 1300 I Street, N.W., Washington, D.C. 20005-3315.
17.  Recognize as associate attorney \_\_\_\_\_  
(name, address & Reg. No.)
18.  Also enclosed is Declaration of Stanley Marcus, Request for Certified Abstract of Title, Offer to Surrender, Assent of Assignee to Reissue, Reissue Declaration Under 37 C.F.R. § 1.175, Declaration and Power of Attorney, Assignment, Certificate Under 37 C.F.R. § 3.73(b), Information Disclosure Statement and PTO Form 1449.

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**PETITION FOR EXTENSION.** If any extension of time is necessary for the filing of this application, including any extension in the parent application, serial no. 08/544,212, filed October 17, 1995, for the purpose of maintaining copendency between the parent application and this application, and such extension has not otherwise been requested, such an extension is hereby requested, and the Commissioner is authorized to charge necessary fees for such an extension to our Deposit Account No. 06-0916. A duplicate copy of this paper is enclosed for use in charging the deposit account.

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GARRETT & DUNNER, L.L.P.

By: Robert J. Eichelburg  
Robert J. Eichelburg  
Reg. No. : 23, 057

Dated: April 7, 1999

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PATENT  
Attorney Docket No. 1222.0034-01000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

**PRELIMINARY AMENDMENT PURSUANT TO 37 C.F.R. § 1.111  
AND COMMUNICATION PURSUANT TO § 1.177**

Applicants pursuant to 37 C.F.R. § 1.177, hereby submit this 37 C.F.R. § 1.53(b) divisional application from reissue application 08/544,212, filed October 17, 1995. Applicants hereby make this request since the Examiner in the parent reissue application indicated he would not enter claims 61-64 of applicants' February 12, 1999 Amendment in the reissue application.

Please amend the application as follows:

**IN THE CLAIMS:**

1. (Amended Once) A process for forming an oxide composition comprising oxidizing a gaseous composition at a temperature below about 200°C at atmospheric

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pressure, adapted to deposit at least a first layer of an oxide and silicon oxide onto glass at a rate of deposition greater than about 350 Å/sec. wherein the composition comprises a precursor of tin oxide, a precursor of silicon oxide of formula  $R_mO_nSi_p$ , where m is from 3 to 8, n is from 1 to 4, p is from 1 to 4, and R is independently chosen from hydrogen and acyl, straight, cyclic, or branched-chain alkyl and substituted alkyl or alkenyl of from one to about six carbons, and phenyl or substituted phenyl, an accelerant selected from the group consisting of organic phosphites, organic borates and water, and mixtures thereof, and a source of oxygen.

Claim 2. (Amended Once) The [gaseous composition] process of claim 1, adapted to deposit at least a first layer comprising tin oxide and silicon oxide onto transparent flat glass at a temperature of from 450° to about 650°C.

Claim 3. (Amended Once) The [gaseous composition] process of claim 1, adapted to deposit at least a first layer comprising tin oxide and silicon oxide onto transparent flat glass to produce a glass article having essentially no reflected color in daylight.

Claim 4. (Amended Once) The [gaseous composition] process of claim 1 adapted to continuously deposit at least a first layer of tin oxide and silicon oxide onto a continuously moving transparent flat glass substrate.

Claim 5. (Amended Once) The [composition] process of claim 1 at a temperature below about 175°C.

Claim 6. (Amended Once) The [composition] process of claim 1 wherein the organic phosphite and organic borate accelerants have the formula  $(R''O)_3P$  and

(R"O)<sub>3</sub>B where R" is independently chosen from straight, cyclic or branched-chain alkyl or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or R'" CH<sub>2</sub>CH<sub>2</sub>-, where R''' is MeO<sub>2</sub>C-, EtO<sub>2</sub>C-, CH<sub>3</sub>CO-, or HOOC-.

Claim 7. (Amended Once) The [composition] process of claim 1 wherein the precursor of the tin oxide is R<sub>n</sub>SnX<sub>4-n</sub>, where R is a straight, cyclic, or branched-chain alkyl, or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or R'CH<sub>2</sub>CH<sub>2</sub>-, where R' is MeO<sub>2</sub>C-, EtO<sub>2</sub>C-, CH<sub>3</sub>CO-, or HO<sub>2</sub>C-; X is selected from the group consisting of halogen, acetate, perfluoroacetate, and their mixtures; and where n is 0, 1, or 2.

Claim 8. (Amended Once) The [composition] process of claim 1 wherein the precursor of the tin oxide is an alkyltin halide.

Claim 9. (Amended Once) The [composition] process of claim 1 wherein the precursor of the tin oxide is an alkyltin chloride.

Claim 10. (Amended Once) The [composition] process of claim 1 wherein the precursor of tin oxide is chosen from the group consisting of monobutyltin trichloride, dibutyltin dichloride, tributyltin chloride, and tin tetrachloride.

Claim 11. (Amended Once) The [composition] process of claim 1 wherein the precursor of silicon oxide is selected from the group consisting of tetraethylorthosilicate, diacetoxymethylsilane, ethyltriacetoxysilane, methyltriacetoxysilane, methyldiacetoxysilane, tetramethyldisiloxane, tetramethylcyclotetrasiloxane, dipinacoloxysilane, 1,1-dimethylsila-2-oxacyclohexane, tetrakis (1-methoxy-2-propoxy) silane, and triethoxysilane.

Claim 12. (Amended Once) The [composition] process of claim 1 wherein the precursor of silicon oxide is tetraethylorthosilicate.

Claim 13. (Amended Once) The [composition] process of claim 1 wherein the accelerator comprises triethyl phosphite.

Claim 14. (Amended Once) The [composition] process of claim 1 wherein the accelerator comprises triethyl phosphite and triethyl borate.

Claim 15. (Amended Once) The [gaseous combination] process of claim 1 adapted to deposit at least a first layer of tin oxide and silicon oxide onto glass at a rate of deposition greater than about 400 Å/sec.

Claim 16. (Amended Once) The [gaseous composition] process of claim 1 adapted to deposit at least a first amorphous layer of tin oxide and silicon oxide onto glass.

Claim 17. (Amended Once) The [gaseous composition] process of claim 1 adapted to deposit a plurality of layers comprising tin oxide and silicon oxide onto glass, the outermost layer of which is further adapted for deposit of at least a second layer.

Claim 18. (Amended Once) The [composition] process of claim 17 adapted to deposit a plurality of layers comprising tin oxide and silicon oxide onto glass, the outermost layer of which is further adapted for deposit of a layer comprising tin oxide.

Claim 19. (Amended Once) The [composition] process of claim 17 adapted to deposit a plurality of layers comprising tin oxide and silicon oxide onto glass, the outermost layer of which is further adapted for deposit of a layer comprising tin oxide and fluorine.

Claim 20. (Amended Once) The [composition] process of claim 17 wherein the second layer comprises a doped tin oxide.

Claim 21. (Amended Once) The [composition] process of claim 17 wherein said plurality of layers are deposited from a precursor mixture comprising monobutyltin trichloride, tetraethyl orthosilicate and triethyl phosphite.

Claim 22. (Amended Once) The [composition] process of claim 1 adapted to deposit at least a first layer comprising tin oxide and silicon oxide onto glass, said first layer having a refractive index which changes continuously between the glass substrate and the top of the layer.

Claim 23 (Amended Once) A process for forming an oxide composition comprising oxidizing a gaseous composition at a temperature below about 200°C at atmospheric pressure, adapted to deposit at least a first amorphous layer comprising tin oxide and silicon oxide onto glass at a rate of deposition greater than about 400 Å/sec., the layer having a controlled index of refraction, wherein the composition comprises a tin oxide precursor, a silicon oxide precursor of formula R<sub>m</sub>O<sub>n</sub>Si<sub>p</sub>, where m is from 3 to 8, n is from 1 to 4, p is from 1 to 4, and R is independently chosen from hydrogen and acyl, straight, cyclic, or branched-chain alkyl and substituted alkyl or alkenyl of from one to about six carbons, and phenyl or substituted phenyl, and at least one accelerant chosen from the group consisting of boron and phosphorous esters and water.

Claim 24. (Amended Once) The [gaseous composition] process of claim 23 adapted to continuously deposit at least a first layer comprising tin oxide and silicon

oxide onto a continuously moving flat glass substrate at a temperature of from about 450° to about 650°C, and comprising monobutyltin trichloride, tetraethyl orthosilicate and an accelerator.

Claim 25. (Amended Once) A process for forming an oxide composition comprising oxidizing a gaseous composition at a temperature below about 200°C and at atmospheric pressure, adapted to deposit at least a first layer comprising amorphous tin oxide and silicon oxide onto glass at a temperature of from about 450° to 650°C at a rate of deposition greater than about 350 Å/sec. wherein the composition comprises:

a tin oxide precursor of formula  $R_nSnX_{4-n}$ , where R is a straight, cyclic, or branched-chain alkyl, or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or  $R'CH_2CH_2-$ , where  $R'$  is  $MeO_2C-$ ,  $EtO_2C-$ ,  $CH_3CO-$ , or  $HO_2C-$ ; X is selected from the group consisting of halogen, acetate, perfluoroacetate, and their mixtures; and where n is 0, 1, or 2;

a silicon oxide precursor of formula  $R_mO_nSi_p$ , where m is from 3 to 8, n is from 1 to 4, p is from 1 to 4, and R is independently chosen from hydrogen and acyl, straight, cyclic, or branched-chain alkyl and substituted alkyl or alkenyl of from one to about six carbons, and phenyl or substituted phenyl;

one or more accelerants selected from the group consisting of water and organic phosphites and organic borates of formula  $(R''O)_3P$  and  $(R''O)_3B$  where  $R''$  is independently chosen from straight, cyclic or branched-chain alkyl or

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alkeynl of from one to about six carbons; phenyl, substituted phenyl, or R'" CH<sub>2</sub>CH<sub>2</sub>—, where R'" is MeO<sub>2</sub>C—, EtO<sub>2</sub>C—, CH<sub>3</sub>CO—, or HOOC—; and a source of oxygen.

Claim 26. (Amended Once) A [composition] process according to claim 25 in which the precursor of the tin oxide is an alkyltin halide, the precursor of the silicon oxide is tetraethylorthosilicate, diacetoxymethyl-t-butoxysilane, ethyltriacetoxysilane, methyltriacetoxysilane, methyldiacetoxysilane, tetramethyldisiloxane, tetramethylcyclotetrasiloxane, dipinacoloxysilane, 1,1-dimethylsila-2-oxacyclohexane, tetrakis (1-methoxy-2-propoxy) silane, or triethoxysilane, and the accelerator comprises one or both of triethyl phosphite and triethyl borate.

Claim 27. (Amended Once) A [composition] process according to claim 26 in which the tin oxide precursor comprises monobutyltin trichloride, the silicon oxide precursor comprises tetraethyl orthosilicate and the accelerator comprises triethyl phosphite.

Claim 28. (Amended Once) A process for forming an oxide composition comprising oxidizing a gaseous composition comprising at least one precursor of a metal oxide and an accelerator selected from the group consisting of organic phosphites, organic borates, and water.

Claim 29. (Amended Once) The process of claim 28 wherein at least one precursor for a metal oxide is selected from the group consisting of compounds of tin, germanium, titanium, aluminum, zirconium, zinc, indium, cadmium, hafnium, tungsten, vanadium, chromium, molybdenum, iridium, nickel, and tantalum.

Claim 30. (Amended Once) The process of claim 28 further comprising a precursor for a silicon oxide.

Claim 31. (Amended Once) A process for forming an oxide composition comprising oxidizing a gaseous composition comprising a metal oxide precursor and an accelerant selected from the group consisting of phosphites, borates, water, alkyl phosphine, arsine and borane derivatives, PH<sub>3</sub>, AsH<sub>3</sub>, B<sub>2</sub>H<sub>6</sub>, O<sub>2</sub>, N<sub>2</sub>O, NF<sub>3</sub>, NO<sub>2</sub> and CO<sub>2</sub>.

Claim 32. (Amended Once) The process of claim 31 wherein the metal oxide precursor is a precursor of metal oxides selected from the group consisting of tin oxide, germanium oxide, titanium oxide, aluminum oxide, zirconium oxide, zinc oxide, indium oxide, cadmium oxide, hafnium oxide, tungsten oxide, vanadium oxide, chromium oxide, molybdenum oxide, iridium oxide, nickel oxide, and tantalum oxide.

Please cancel claims 33-49 without prejudice and add the following new claims:

- 50. A product produced by the process of any one of claims 1-32.
- 51. A product produced by the process of any one of claims 1-32 wherein said oxidizing is effected in a chemical vapor deposition process.--

#### REMARKS

Claims 61-64 of Applicants' February 12, 1999 Amendment in the parent application, which the Examiner indicated he would not enter, comprise process and product by process claims. These claims have been replaced by new claims 1-32 and

50-51 which comprise process and product by process claims which the originally filed claims in the great-grandparent, grandparent and parent application support.<sup>1</sup>

For example, the claims of the great-grandparent application comprise composition claims for coating a substrate with at least one metal-oxide precursor and at least one deposition-rate enhancing material. Claim 1 of the grandparent application claims a method of depositing a film onto a substrate which comprises depositing at least one layer in the presence of at least one deposition-rate enhancing substance. Claim 6 describes the layer as comprising metal and silicon oxides. Claim 1 of the parent application describes a gaseous composition for the deposition of a layer of tin oxide and silicon oxide onto glass at a deposition-rate greater than about 350 Å/sec. All of these claims clearly show an intent to claim the process and product produced by the process which the claims now cover.

The present amendment amends claims 1-32, originally describing a gaseous composition so that they now claim a process for oxidizing a gaseous composition. Claims 50 and 51 claim the product produced by that process.

Applicants have filed the present application in view of the Examiner's position of refusing to enter process and product by process claims 61-64, in the reissue application as not drawn to an invention under consideration. To the extent this comprises a restriction requirement, applicants point out that MPEP § 1450 provides "[t]he examiner may **not** require restriction in a reissue application (37 C.F.R. 1.176 and

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<sup>1</sup> Exhibits 1, 2 and 3 attached to applicants' March 14, 1998 Amendment in reissue application Serial No. 08/544,212 comprise the claims of the great grandparent, grandparent and parent applications of the reissue application.

MPEP § 1440). Even where the original patent contains claims to different inventions which the examiner considers independent and distinct, and the reissue application claims the same inventions, the examiner should not require restriction between them or take any other action with respect to the question of plural inventions. Restriction may only be requested by the applicant (37 C.F.R. § 1.177 and MPEP §1451). . ." (Emphasis in original). Applicants therefore have filed the present application to cover the subject matter of claims 61-64 in a separate application.

If filing this communication requires payment of a fee which this communication fails to account for, applicants' attorneys request charging such fees to their deposit account number 06-0916.

Respectfully submitted,

By:   
Robert J. Eichelburg  
Reg. No. 23,057

Dated: April 7, 1999

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## **COATING COMPOSITION FOR GLASS**

**David A. Russo, Norristown; Ryan R.  
Dirkx, Glenmoore, both of Pa.;  
Glen P. Florczak, East Brunswick,  
N.J.**

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CROSS-REFERENCE TO RELATED  
APPLICATION

This application is a reissue of U.S. Patent No. 5,401,305, issued March 28, 1995 from U.S. Serial No. 104,125, filed December 13, 1993.

This application is a continuation-in-part of our U.S. patent applications, Ser. Nos. 07/814,366, now abandoned, filed Dec. 26, 1991, and 07/814,352, now abandoned, filed Dec. 27, 1991, and a PCT national stage filing under 35 U.S.C. 371 of PCT/US92/10873.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is in the field of coatings on substrates. More particularly, this invention is in the field of compositions for the deposition of coatings at high rates on glass or glass articles to provide controlled refractive index, improved emissivity characteristics, and/or appearance and abrasion resistance, and to complement or enhance other properties.

2. Description of the Prior Art

Transparent semi-conductor films such as indium oxide, cadmium stannate, or doped tin oxide, can be applied to various transparent substrates such as, e.g., soda-lime glasses, in order to reflect long-wavelength infrared radiation. Transparent dielectric films such as titanium dioxide or undoped tin oxide can be applied to transparent articles such as glass bottles to form a base coat for a second coating with a specific function. Depending on the thickness of the semiconductor or dielectric film, various reflected iridescent colors may be observed. This iridescent effect is considered to be detrimental to the appearance of the glass in applications such as windows with low emissivity, or bottles for food or beverages.

Methods and apparatus for coating glass, and especially continuous coating on moving glass, are known in the art. A description of apparatus useful in preparing a coated-glass article is found in Lindner, U.S. Pat. No. 4,928,627, made a part of this disclosure by reference herein.

Various procedures have been devised for reducing or eliminating iridescence. For the low-emissivity application, Zaromb, in U.S. Pat. No. 3,378,396, describes an article comprising a transparent glass substrate coated with tin and silicon oxides; the coating varies gradually in composition from a high ratio of silicon oxide to tin oxide; at the substrate surface, gradually changing to almost pure tin oxide, and changing further to a ratio of not more than 60% silicon oxide to not less than 40% tin oxide at the interface of that coating with the atmosphere. The refractive index of the coating nearest to the substrate is about 1.5, substantially the refractive index of silica glass, and changes to about 2.0, the refractive index of tin oxide, at the air interface, providing

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an intermediate coating layer without an optical interface. The article so coated has little to no iridescence in reflected light. Zaromb teaches that aqueous solutions of tin and silicon chlorides can be spray-applied to achieve his coatings. Spray applications are usually batch operations which do not yield high-quality, uniform films; there is no mention of other means of application such as chemical-vapor deposition (CVD). He also fails to give any indication of the deposition rate, a key parameter for a commercial industrial application.

Another approach is described by Gordon in U.S. Pat. No. 4,187,336. One or more layers of a transparent material with a refractive index intermediate between that of a glass substrate and a conductive tin oxide film are deposited by atmospheric-pressure CVD between the glass and the tin oxide film. It is necessary for the intermediate layers to have specific refractive indices and thicknesses in order to be effective. It is noted that when the intermediate films contained silicon dioxide, suitable volatile compounds were found to be silane, dimethylsilane, diethylsilane, tetramethyl silane, and the silicon halides. No other precursors are mentioned. The deposition rates obtained for the processes described were on the order of from 10 to 20 Angstroms per second ( $\text{\AA/sec.}$ ). Such rates are an order of magnitude below those necessary for a commercial industrial process.

In U.S. Pat. No. 4,206,252, Gordon describes a process for depositing mixed oxide and nitride coating layers of continuously varying refractive index between a glass substrate and an infra-red-reflecting coating, whereby the film iridescence is eliminated. When silicon dioxide is part of the mixed oxide film, the patent teaches that volatile silicon compounds with Si—Si and Si—H bonds are suitable precursors. Compounds such as 1,1,2,2-tetramethylsilane, 1,1,2-trimethylsilane, and 1,2-dimethylsilane are disclosed. All of the compounds containing Si-Si and Si-H bonds to which reference is made are expensive, and none are commercially available.

In U.S. Pat. No. 4,386,117, Gordon describes a process for preparing mixed silicon oxide/tin oxide coatings all specific refractive indices or a continuous gradient as taught by Zaromb in U.S. Pat. No. 3,378,396, at optimum deposition rates of 80 to 125  $\text{\AA/sec.}$ , using alkoxy-alkylpolysilane precursors such as methoxy-phenylmethyldisilane or dimethoxytetramethylsilane. Again, the silica precursors cited and inferred are impractical for industrial use, because none of them is commercially available on a large scale.

Legendijk, in U.S. Pat. No. 5,028,566, notes in column 4 that tetraethyl orthosilicate (TEOS) suffers from a number of disadvantages in its application to a substrate by low-pressure CVD; that is, a pressure of about 500 milliTorr. These disadvantages include difficulty of doping the resultant film with phosphorus, and controlled-source delivery due to the low vapor pressure of TEOS. Legendijk also points out that attempts at an all-liquid process to produce borophosphosilicate glass have met with limited success. He further equates the

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dopant effect within a broad range of phosphorus, boron, antimony, arsenic and chromium compounds, but only when used with silicon compounds having no carbon-oxygen-silicon bonds, and two or more silicon atoms.

In bottle applications, the coatings are applied at such low thicknesses, i.e., about 100 Å, that no iridescence is possible. However, the films are not continuous, and this discontinuity makes them unsuitable for other applications. One solution to the discontinuity is to deposit thicker films of a material with a refractive index closer to that of the article. A mixed metal oxide/silicon oxide material deposited at a significantly more rapid rate than has heretofore been achieved would be desirable, as discussed further hereinbelow.

All the silanes disclosed in the prior art for making mixed metal oxide/silicon dioxide coatings have certain features which make them unsatisfactory for commercial development. Some are very corrosive, flammable, or oxygen-sensitive, and require special handling. Others are not readily available, or are too expensive for commercial use. Of the materials which can be used, the biggest problem which limits their commercial development in mixed metal oxide/silicon oxide and/or oxynitride intermediate layers has been that of inadequate deposition rates. When the substrate is flat glass and the deposition process is CVD at ambient pressure, the deposition rate of the intermediate layers must be high enough to coat a production-line glass ribbon traveling at line speeds as high as about 15 meters per minute (m/min). Rates for deposition of the desired layers of about 350 Å are desirable, and rates on the order of 400 to 600 Å/sec are preferable. Such rates have not heretofore been achieved under conditions which permit continuous, mass production of glass with properties.

To overcome the problems as discussed hereinabove, silica precursors are needed which are inexpensive, readily available, easy to handle, and have adequate deposition rates when vaporized with metal oxide precursors. Alkoxy silanes such as TEOS, a commodity chemical, would be desirable. However, prior to the present invention, it has not been possible to deposit silicon oxide films from TEOS by atmospheric-pressure CVD at commercially acceptable deposition rates, except at temperatures at or above 700 degrees Celsius (°C.). Some success has been achieved at temperatures of from about 450° to about 680° C., but only by modifying the atmospheric-pressure CVD process through plasma enhancement or reduced pressure, neither of which is generally acceptable for commercial use on a continuous glass ribbon. Additives such as oxygen, ozone, or trimethyl phosphite have also been used in these modified processes, but the rates achieved are still lower than those needed for an effective commercial system.

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D. S. Williams and E. A. Dein, in *J. Electrochem. Soc.* 134(3) 657-64 (1987), showed that phosphosilicate and borophosphosilicate glass films with controllable refractive index can be deposited at rates of about 200 Å/sec between 515° and 680° C. by the low-pressure CVD of TEOS with phosphorous or boron oxides in concentrations which varied as a function of the additive used. The low-pressure process described here is not amenable to a continuous on-line application of oxides.

In *Proceedings, 2nd International ULSI Science and Technical Symposium, ECS Proceedings* Vol. 98(9), 571-78 (1989), D. A. Webb et al. reported that silicon oxide films could be deposited from TEOS at rates of about 125 Å/sec in a plasma-enhanced CVD process using oxygen. However, plasma-enhanced CVD is not a viable option for the continuous commercial application of oxide films to glass, being a batch process requiring complex and costly low-pressure apparatus.

A. K. Hochberg and D. L. O'Meara in *J. Electrochem. Soc.* 136(6) 1843 (1989) reported enhanced deposition of silicon oxide films at 570° C. by CVD at low pressure when trimethylphosphite was added to TEOS. As with plasma-enhanced CVD, however, low-pressure CVD is not readily utilized for the continuous commercial application of silicon-oxide films on a moving glass sheet to produce a coated-glass article, due at least in part to the cost and complexity of the device used for deposition at low pressure.

From a review of the prior art, it cannot be determined what precursor combinations, if any, can be used for continuous deposition, under conditions and at a rate suitable for mass production, of mixed metal oxide/silicon oxide films at adequate rates from readily available and relatively inexpensive reagents.

Primary or secondary coatings on glass substrates are further useful to enhance or complement properties of either the substrate or one or more of the coatings thereon, improvement of iridescence being only one application. Other uses of coatings include, e.g., protection of the substrate surface from abrasion, addition of color to clear glass, and screening of particular wavelengths of incident radiation.

#### DISCUSSION OF THE INVENTION

This invention is a gaseous composition for producing an improved coating on glass, wherein the coated glass exhibits specific properties such as, e.g., controlled refractive index, abrasion resistance, color enhancement, low emissivity, selective light filtration, and anti-iridescence on flat-glass substrates. The invention is made by CVD at rates greater than about 350 Å/sec. at atmospheric pressure and at temperatures lower than 700° C., by using a mixture which includes at least one precursor for a metal oxide, selected from the group consisting of volatile compounds of tin, germanium, titanium, aluminum, zirconium, zinc, indium, cadmium, hafnium, tungsten, vanadium, chromium, molybdenum, indium, nickel and tantalum. The gaseous composition further includes a precursor for silicon dioxide, and one or more additives selected from the group consisting of phosphites, borates, water, alkyl phosphine, arsine and

borane derivatives; PH<sub>3</sub>, AsH<sub>3</sub> and B<sub>2</sub>H<sub>6</sub>; and O<sub>2</sub>, N<sub>2</sub>O, NF<sub>3</sub>, NO<sub>2</sub> and CO<sub>2</sub>. The additives are termed "accelerants" herein; the accelerants serve to increase the rate of deposition of the film onto the glass from the mixture. The mixture of precursors and additives is gaseous under the conditions of application required to produce the coated-glass article; the reaction of the materials in the gaseous mixture with atmospheric or added oxygen provides the corresponding oxides which are deposited on the glass substrate.

Those skilled in the art will understand that precursors and materials discussed in this specification must be sufficiently volatile, alone or with other materials, and sufficiently stable under the conditions of deposition, to be a part of the composition from which the desired films are deposited.

Precursors for deposition of metal oxides include, e.g., aluminum alkyls and alkoxides, cadmium alkyls, germanium halides and alkoxides, indium alkyls, titanium halides, zinc alkyls, and zirconium alkoxides. Specific examples of such compounds include, e.g., Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, CrO<sub>2</sub>Cl<sub>3</sub>, GeBr<sub>4</sub>, Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, TiCl<sub>4</sub>, TiBr<sub>4</sub>, Ti(C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>)<sub>4</sub>, Zr(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, Ni(CO)<sub>4</sub>, VCl<sub>4</sub>, Zn(CH<sub>3</sub>)<sub>2</sub>, Zr(C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>)<sub>4</sub>, and the like.

Tin precursors include those described by the general formula R<sub>n</sub>SnX<sub>4-n</sub>, where R is independently chosen from straight, cyclic, or branched-chain alkyl or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or R'CH<sub>2</sub>CH<sub>2</sub>—, where R' is MeO<sub>2</sub>C—, EtO<sub>2</sub>C—, CH<sub>3</sub>CO—, or HO<sub>2</sub>C—; X is selected from the group consisting of halogen, acetate, perfluoroacetate, and their mixtures; and where n is 0, 1, or 2. Preferred precursors for tin oxide in the article of this invention are the organotin halides.

Precursors for silicon oxide include those described by the general formula R<sub>m</sub>O<sub>n</sub>Si<sub>p</sub>, where m is from 3 to 8, n is from 1 to 4, p is from 1 to 4, and R is independently chosen from hydrogen and acyl, straight, cyclic, or branched-chain alkyl and substituted alkyl or alkenyl of from one to about six carbons, and phenyl or substituted phenyl. Preferred precursors for silicon oxide include tetraethylorthosilicate, diacetoxymethylbutoxysilane, ethyltriacetoxysilane, methyltriacetoxysilane, methyldiacetoxysilane, tetramethyldisiloxane, tetramethylcyclotetrasiloxane, dipinacoloxysilane, 1,1-dimethylsila-2-oxacyclohexane, tetrakis (1-methoxy-2-propoxy) silane, and triethoxysilane.

Suitable accelerants include phosphite and borate derivatives of the general formula (R''O)<sub>3</sub>P and (R''O)<sub>3</sub>B, where R'' is independently chosen from straight, cyclic, or branched-chain alkyl or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or R'''CH<sub>2</sub>CH<sub>2</sub>—, where R''' is MeO<sub>2</sub>C—, EtO<sub>2</sub>C—, CH<sub>3</sub>CO—, or HO<sub>2</sub>C—; R'' is preferably alkyl or alkenyl of from 1 to 4 carbons in length. Particularly preferred accelerants are those selected from the group consisting of boron and phosphorus esters; most preferred are TEB and TEP.

The precursors to the overcoated layer comprise MBTC or any of the organotins described by the general formula R<sub>n</sub>SnX<sub>4-n</sub>, above, and a material chosen to impart a semi-conductive property to the tin oxide; such materials include, e.g., antimony compounds such as

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trimethylantimony, phosphorous compounds such as triethylphosphine, and fluorine-containing compounds such as trifluoroacetic acid, trifluoroacetic anhydride, ethyl trifluoroacetate, 2,2,2-trifluoroethanol, ethyl 4,4,4-trifluoroacetoacetone, heptafluorobutyryl chloride, and hydrogen fluoride. The tin oxide layer can also be made conductive by depositing sub-stoichiometric films having the composition  $\text{SnO}_2 - x$ , wherein  $x$  is a non-integer having a value between zero and 1, and wherein the value of  $x$  can vary within a given film. The materials for imparting semi-conductive properties to the tin oxide can also be added to the precursors for the first layer, to enhance the emissivity of the entire coating system, i.e., the emissivity of the combined first and second layers.

Those skilled in the art will realize that the tin oxide can be replaced in these films entirely or in part by the oxides of other metals such as, e.g., germanium, titanium, aluminum, zirconium, zinc, indium, cadmium, hafnium, tungsten, vanadium, chromium, molybdenum, iridium, nickel and tantalum.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred embodiment of the present invention is a gaseous composition at a temperature below about 200° C. at atmospheric pressure, adapted to deposit a film of tin oxide and silicon oxide at a rate greater than about 350 Å/sec. which comprises a precursor of tin oxide, a precursor of silicon oxide, an accelerant selected from the group consisting of organic phosphites, organic borates and water, and mixtures thereof, and a source of oxygen.

In another embodiment of this invention, the composition results in a film deposited at atmospheric pressure wherein the film comprises one or more mixed metal oxide/silicon dioxide films on a glass substrate, the deposition being made from a mixture comprising a metal oxide precursor, a silicon dioxide precursor, and at least one additive which improves or accelerates the deposition rate significantly when compared to the deposition rate without the additive. The deposited films can contain additional oxides related to the additives used. Further, the deposited mixed oxide films can have specific properties in their own right such as, e.g., designed refractive index, or can be combined with other films, under- or overcoated, or both, to have a combined property such as, e.g., color neutrality or lubricity.

In a more-preferred embodiment, the composition provides a mixed metal oxide/silicon dioxide film comprising multiple tin oxide/silicon dioxide layers of, e.g., increasing refractive index; further, a chosen property of a given layer, such as, e.g., the refractive index, can vary continuously such that an overcoated layer of tin oxide will have minimal reflected color. A given layer may thus have a concentration of silicon oxide and tin oxide different from the concentrations of silicon oxide and tin oxide in an adjacent layer. The films can also contain oxides of the accelerants, particularly when the additives contain phosphorus or boron.

In a most-preferred embodiment of the composition of this invention, the precursors to the mixed oxide

layer comprise organotin halides generally and monoburyltin trichloride (MBTC) in particular, TEOS, and the accelerant triethyl phosphate (TEP).

The compositions of the films produced by this invention were determined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The article of the present invention is prepared by a process using accelerants whereby the process provides a commercially acceptable continuous CVD deposition of oxide films on moving glass, especially on a modern float-glass line, where the batch processes of the prior art are entirely inapplicable.

The effects of added water and added phosphites and borates on the refractive index and deposition rate of TEOS-based mixed oxide films are shown in the following Tables. These results are contrasted to those in Tables IV and V, which show the effect of the additives oxygen and a Lewis acid.

Table I shows the effect of added water. As the water concentration is increased, regardless of the tin/silicon ratio or the gas velocity, the deposition rate increases to commercially significant levels. These rate increases are also accompanied by increases in refractive index. In the tables here, the reported deposition rates are approximate with a range of about seven percent, unless the rate is followed by an expressed  $\pm$  uncertainty.

TABLE I

Effect of Water Concentration on Mixed Oxide Refractive Index and Deposition Rate				
MBTC mol %	TEOS mol %	Water mol %	R.I.	Dep. Rate Å/sec
665° C. glass temperature, 160° C. system temperature, 50 l/min gas flow.				
0.71	0.71	0.00	1.54	25
0.71	0.71	0.15	1.73	340
0.71	0.71	0.24	1.74	400
665° C. glass temperature, 160° C. system temperature, 12.5 l/min gas flow.				
1.05	0.59	0.00	1.74	290
1.05	0.59	0.60	1.78	330
1.05	0.59	1.10	1.80	480

While 160° C. is preferred, the system temperature can be from about 125° to about 200° C.

Table II shows the effects of added TEP and of mixtures of TEP and lower-alkyl borate esters such as triethyl borate (TEB). The results show that TEP is very effective in accelerating the deposition rates of the mixed-oxide films to a high rate at specific and controlled refractive-index values. Additions of TEB at low levels to the TEP resulted in an additional small increase in rate. As used in this specification, the term "high rate," as applied to the film deposition described herein, is greater than about 350 Å/sec, and preferably about 400 Å/sec or higher. All the films produced under the conditions of Table II were clear.

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TABLE II

Effect of MBTC/TEOS/TEP Concentrations on Deposition Rate

% TEOS	% MBTC	% TEP	% TEB	R.I.	Dep. Rate Å/sec
0.80	0.16	—	—	1.69 ± .02	38 ± 3
0.80	0.11	0.76	—	1.58 ± .01	542 ± 3
0.80	0.16	0.76	—	1.60 ± .01	416 ± 22
0.78	.56	0.73	—	1.67 ± .01	505 ± 4
0.78	1.34	0.75	—	1.69 ± .01	476 ± 45
0.78	1.56	0.76	—	1.73 ± .01	231 ± 46
0.27	1.56	0.62	—	1.71 ± .01	181 ± 15
0.27	1.56	0.73	—	1.70 ± .01	482 ± 6
0.27	1.56	0.75	—	1.70 ± .01	482 ± 16
0.27	1.56	0.74	0.18	1.70 ± .02	492 ± 13
0.79	> 0.16	0.76	0.19	1.59 ± .01	473 ± 56

The glass temperature was 665° C., its speed, 0.56 m/sec; system temperature 160° C., air. MBTC, TEOS, and TEP or the mixture of TEP and TEB were injected separately into the vaporizer section of the coater. Each data point was the average of three samples. The dew point was from -74° to -78° C.

Table III shows the effect of added oxygen. Increasing the oxygen concentration increases the deposition rate significantly, but not to the levels needed for commercial application.

TABLE III

Effect of Oxygen Concentration On Mixed Oxide Refractive Index and Deposition Rate

MBTC mol %	TEOS mol %	Oxygen vol % of air	R.I.	Dep. Rate Å/sec
0.71	0.71	20	1.54	25
0.71	0.71	50	1.63	50
0.71	0.71	75	1.65	160
0.71	0.71	100	1.66	240

665° C. glass temperature, 160° C. system temperature, 50 l/min gas flow.

Table IV shows the effect of added Lewis acid, which in this case is excess MBTC. As the concentration increases, the rate increases, although not to the levels needed for commercial application.

TABLE IV

Effect of MBTC Concentration on Mixed Oxide Refractive Index and Deposition Rate

MBTC mol %	TEOS mol %	R.I.	Dep. Rate Å/sec
0.48	0.47	1.78	160
0.48 ± 0.23	0.48	1.78	200
0.48 ± 0.47	0.47	1.85	300

665° C. glass temperature, 160° C. system temperature, 50 l/min gas flow.

The data in the tables show that effective CVD of mixed oxide films can be achieved at commercial rates by the present invention, with concomitant control of refractive index. The following examples illustrate preferred embodiments of this invention.

#### EXAMPLE 1

A square plate of soda-lime silica glass, 9 centimeters (cm.) on a side, was heated on a hot block to 665° C. A gas mixture of about 0.16 mol % MBTC, 0.80 mol %

TEOS, 0.75 mol % TEP, and the balance hot air at 160° C was directed over the glass at a rate of 12.5 liters per minute (1/min) for about 10 seconds. The center of the glass surface was uniformly coated with a film which had a pale green color in reflected light. Using the Prism Coupler technique, the refractive index was found to be 1.60 and the thickness was about 4260 Å, corresponding to a deposition rate of about 426 Å/sec. Similarly deposited films have been shown to be amorphous by XRD, and to be composed of oxides of tin, silicon and phosphorus by XPS.

#### EXAMPLE 2

A gas mixture of about 1.84 mol % MBTC, 0.78 mol % TEOS, 0.75 mol % TEP, and the balance hot air was directed over a glass surface in the same manner as described in Example 1. The resulting film had a pale magenta color in reflected light. The refractive index was found to be 1.68, and the thickness was about 4930 Å, corresponding to a deposition rate of about 493 Å/sec. Similarly deposited films have been shown to be amorphous by XRD, and to be composed of oxides of tin, silicon and phosphorus by XPS.

#### EXAMPLE 3

A gas mixture of about 1.22 mol % MBTC, 0.58 mol % TEOS, 1.09 mol % H<sub>2</sub>O and the balance hot air was directed over a glass surface as described in Example 1, but for eight seconds. The resulting film had a green color in reflected light. The refractive index was found to be 1.78, and the film thickness was about 4650 Å, which corresponds to a deposition rate of about 580 Å/sec. From XRD analysis, similarly deposited films have been found to consist of collapsed tetragonal unit cells of tin oxide, indicating some solid-solution formation with silicon dioxide. XPS analysis shows that the films comprise oxides of tin and silicon.

#### EXAMPLE 4

Each of the films described in Examples 1 through 3 was successively deposited for one second in ascending-index order. The multi-layer film was then overcoated with about 3200 Å of fluorine-doped tin oxide. This film construction provided a transparent article with essentially no reflected color under conditions of daylight illumination.

#### EXAMPLE 5

A 9-cm. square of soda-lime silica glass was heated on a hot block to 665° C. A gas mixture of about 1.04 mol % MBTC in air at 160° C., and a gas mixture of 1.04 mol % TEOS and 0.20 mol % TEP in air at 160° C. were directed through two microprocessor-controlled globe valves over the glass at a total flow rate of 12.5 l/min for 30 sec. The globe valves were simultaneously opened and closed at a programmed rate such that the gas composition impinging on the glass sample was continuously changed from a mixture of high TEOS/TEP and low MBTC to a mixture of low TEOS/TEP and high MBTC. The center of the glass surface was uniformly coated with a film consisting of oxides of tin,

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silicon and phosphorus as determined by XPS analysis. As the film thickness increased, the amount of tin gradually increased, while the amount of silicon and phosphorus decreased. The refractive index was calculated from these data, and from data derived from standard films, and found to lie between 1.52 and 1.87. This film construction provided an article with essentially no reflected color when overcoated with fluorine-doped tin oxide.

#### EXAMPLE 6

A gas mixture of about 0.16 mol % MBTC, 0.80 mol % TEOS, and the balance hot air was directed over a glass surface as described in Example 1 for about 60 seconds. The resulting film had a magenta color in reflected light, and a refractive index of 1.69. The film thickness was about 2260 Å, corresponding to a deposition rate of about 38 Å/sec.

#### EXAMPLE 7

A 0.5-l clear-glass beverage bottle was rotated and heated to about 600° C. in an oven over a three-minute period. The heated bottle was transferred into a coating chamber, where it was contacted with a vapor mixture of 0.16 mol % MBTC, 0.80 mol % TEOS, 0.75 mol % TEP, and the balance hot air at about 170° C. for 10 sec. The resulting film was magenta-blue in color, and was uniformly distributed on the sidewalls of the container from shoulder to base. The deposition rate was estimated to be about 200 Å/sec from the film color, compared to about 50 Å/sec for the bottle coated only with the vapor mixture of MBTC and TEOS.

From a review of the foregoing tables and examples, those skilled in the art will realize that TEB, TEP, and water serve as accelerants in the CVD of oxide films on glass, and that TEP and TEB are synergistic in accelerating the deposition rate of TEOS and MBTC. Accelerants useful in this invention are chosen from the group consisting of borate and phosphite esters, alkyltin halides, and water.

While the composition of the present invention is preferably applied continuously to a moving glass substrate by methods known to those skilled in the art, the composition of this invention also has utility in batch processes. In application under conditions of continuous deposition, the composition is preferably maintained at temperatures below about 200° C., and more preferably below about 175° C., and applied to the glass moving at about 15 meters per second to provide deposition at a rate of at least 350 Å/sec., and preferably at a rate of at least 400 Å/sec.

Modifications and improvements to the preferred forms of the invention disclosed and described herein may occur to those skilled in the art who come to understand the principles and precepts hereof. Accordingly, the scope of the patent to be issued hereon should not be limited solely to the embodiments of the invention set forth herein, but rather should be limited only by the advance by which the invention has promoted the art.

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What is claimed is:

1. A gaseous composition at a temperature below about 200° C. at atmospheric pressure, adapted to deposit at least a first layer of tin oxide and silicon oxide onto glass at a rate of deposition greater than about 350 Å/sec. wherein the composition comprises a precursor of tin oxide, a precursor of silicon oxide of formula  $R_mO_nSi_p$ , where m is from 3 to 8, n is from 1 to 4, p is from 1 to 4, and R is independently chosen from hydrogen and acyl, straight, cyclic, or branched-chain alkyl and substituted alkyl or alkenyl of from one to about six carbons, and phenyl or substituted phenyl, an accelerant selected from the group consisting of organic phosphites, organic borates and water, and mixtures thereof, and a source of oxygen.
2. The gaseous composition of claim 1, adapted to deposit at least a first layer comprising tin oxide and silicon oxide onto transparent flat glass at a temperature of from 450° to about 650° C.
3. The gaseous composition of claim 1, adapted to deposit at least a first layer comprising tin oxide and silicon oxide onto transparent flat glass to produce a glass article having essentially no reflected color in daylight.
4. The gaseous composition of claim 1 adapted to continuously deposit at least a first layer of tin oxide and silicon oxide onto a continuously moving transparent flat glass substrate.
5. The composition of claim 1 at a temperature below about 175° C.
6. The composition of claim 1 wherein the organic phosphite and organic borate accelerants have the formula  $(R''O)_3P$  and  $(R''O)_3B$  where R'' is independently chosen from straight, cyclic or branched-chain alkyl or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or  $R''-CH_2CH_2-$ , where R'' is  $MeO_2C-$ ,  $EtO_2C-$ ,  $CH_3CO-$ , or  $HOOC-$ .
7. The composition of claim 1 wherein the precursor of the tin oxide is  $R_xSnX_{4-n}$ , where R is a straight, cyclic, or branched-chain alkyl, or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or  $R'CH_2CH_2-$ , where R' is  $MeO_2C-$ ,  $EtO_2C-$ ,  $CH_3CO-$ , or  $HO_2C-$ ; X is selected from the group consisting of halogen, acetate, perfluoroacetate, and their mixtures; and where n is 0, 1, or 2.
8. The composition of claim 1 wherein the precursor of the tin oxide is an alkyltin halide.
9. The composition of claim 1 wherein the precursor of the tin oxide is an alkyltin chloride.
10. The composition of claim 1 wherein the precursor of the tin oxide is chosen from the group consisting of monobutyltin trichloride, dibutyltin dichloride, tributyltin chloride, and tin tetrachloride.
11. The composition of claim 1 wherein the precursor of silicon oxide is selected from the group consisting of tetraethylorthosilicate, diacetoxymethylbutoxysilane, ethyltriacetoxysilane, methyltriacetoxysilane, methyl-diacetoxysilane, tetramethyldisiloxane, tetraramethylcyclotetrasiloxane, dipinacoloxysilane, 1,1-dimethyl-sila-2-oxacyclohexane, tetrakis (1-methoxy-2-propoxy) silane, and triethoxysilane.

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12. The composition of claim 1 wherein the precursor of silicon oxide is tetraethylorthosilicate.
  13. The composition of claim 1 wherein the accelerant comprises triethyl phosphite.
  14. The composition of claim 1 wherein the accelerant comprises triethyl phosphite and triethyl borate.
  15. The gaseous composition of claim 1 adapted to deposit at least a first layer of tin oxide and silicon oxide onto glass at a rate of deposition greater than about 400 Å/sec.
  16. The gaseous composition of claim 1 adapted to deposit at least a first amorphous layer of tin oxide and silicon oxide onto glass.
  17. The gaseous composition of claim 1 adapted to deposit a plurality of layers comprising tin oxide and silicon oxide onto glass, the outermost layer of which is further adapted for deposit of at least a second layer.
  18. The composition of claim 17 adapted to deposit a plurality of layers comprising tin oxide and silicon oxide onto glass, the outermost layer of which is further adapted for deposit of a layer comprising tin oxide.
  19. The composition of claim 17 adapted to deposit a plurality of layers comprising tin oxide and silicon oxide onto glass the outermost layer of which is further adapted for deposit of a layer comprising tin oxide and fluorine.
  20. The composition of claim 17 wherein the second layer comprises a doped tin oxide.
  21. The composition of claim 17 wherein said plurality of layers are deposited from a precursor mixture comprising monobutyltin trichloride, tetraethyl orthosilicate and triethyl phosphite.
  22. The composition of claim 1 adapted to deposit at least a first layer comprising tin oxide and silicon oxide onto glass, said first layer having a refractive index which changes continuously between the glass substrate and the top of the layer.
  23. A gaseous composition at a temperature below about 200° C. at atmospheric pressure, adapted to deposit at least a first amorphous layer comprising tin oxide and silicon oxide onto glass at a rate of deposition greater than about 400 Å/sec., the layer having a controlled index of refraction, wherein the composition comprises a tin oxide precursor, a silicon oxide precursor of formula  $R_mO_nSi_p$ , where m is from 3 to 8, n is from 1 to 4, p is from 1 to 4, and R is independently chosen from hydrogen and acyl, straight, cyclic, or branched-chain alkyl and substituted alkyl or alkenyl of from one to about six carbons, and phenyl or substituted phenyl, and at least one accelerant chosen from the group consisting of boron and phosphorous esters and water.
  24. The gaseous composition of claim 23 adapted to continuously deposit at least a first layer comprising tin oxide and silicon oxide onto a continuously moving flat glass substrate at a temperature of from about 450° to about 650° C., and comprising monobutyltin trichloride, tetraethyl orthosilicate and an accelerant.
  25. A gaseous composition at a temperature below about 200° C. and at atmospheric pressure, adapted to deposit at least a first layer comprising amorphous tin

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oxide and silicon oxide onto glass at a temperature of from about 450° to 650° C. at a rate of deposition greater than about 350 Å/sec., wherein the composition comprises:

- a tin oxide precursor of formula  $R_nSnX_{4-n}$ , where R is a straight, cyclic, or branched-chain alkyl, or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or  $R'CH_2CH_2-$ , where  $R'$  is  $MeO_2C-$ ,  $EtO_2C-$ ,  $CH_3CO-$ , or  $HO_2C-$ , X is selected from the group consisting of halogen, acetate, perfluoroacetate, and their mixtures; and where n is 0, 1, or 2;
- a silicon oxide precursor of formula  $R_mO_nSi_p$ , where m is from 3 to 8, n is from 1 to 4, p is from 1 to 4, and R is independently chosen from hydrogen and acyl, straight, cyclic, or branched-chain alkyl and substituted alkyl or alkenyl of from one to about six carbons, and phenyl or substituted phenyl;
- one or more accelerants selected from the group consisting of water and organic phosphates and organic borates of formula  $(R''O)_3P$  and  $(R''O)_3B$  where  $R''$  is independently chosen from straight, cyclic or branched-chain alkyl or alkenyl of from one to about six carbons; phenyl, substituted phenyl, or  $R'''CH_2CH_2-$ , where  $R'''$  is  $MeO_2C-$ ,  $EtO_2C-$ ,  $CH_3CO-$ , or  $HOOC-$ ; and
- a source of oxygen.

26. A composition according to claim 25 in which the precursor of the tin oxide is an alkytin halide, the precursor of the silicon oxide is tetraethylorthosilicate, diacetoxydi-t-butoxysilane, ethyltriacetoxy silane, methyltriacetoxy silane, methyl diacetoxy silane, tetramethyl-disiloxane, tetramethylcyclotetrasiloxane, dipinacoloxysilane, 1,1-dimethylsila-2-oxacyclohexane, tetrakis (1-methoxy-2-propoxy) silane, or triethoxysilane, and the accelerant comprises one or both of triethyl phosphate and triethyl borate.

27. A composition according to claim 26 in which the tin oxide precursor comprises monobutyltin trichloride, the silicon oxide precursor comprises tetraethyl orthosilicate and the accelerant comprises triethyl phosphate.

28. A gaseous composition comprising at least one precursor of a metal oxide and an accelerant selected from the group consisting of organic phosphites, organic borates, and water.

29. The gaseous composition of claim 28, wherein at least one precursor for a metal oxide is selected from the group consisting of compounds of tin, germanium, titanium, aluminum, zirconium, zinc, indium, cadmium, hafnium, tungsten, vanadium, chromium, molybdenum, iridium, nickel, and tantalum.

30. The gaseous composition of claim 28, further comprising a precursor for a silicon oxide.

31. A gaseous composition comprising a metal oxide precursor and an accelerant selected from the group consisting of phosphites, borates, water, alkyl phosphine, arsine and borane derivatives,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{B}_2\text{H}_6$ ,  $\text{O}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NF}_3$ ,  $\text{NO}_2$  and  $\text{CO}_2$ .

32. The gaseous composition of claim 31, wherein the metal oxide precursor is a precursor of metal oxides selected from the group consisting of tin oxide, germanium oxide, titanium oxide, aluminum oxide, zirconium oxide, zinc oxide, indium oxide, cadmium oxide, hafnium oxide, tungsten oxide,

vanadium oxide, chromium oxide, molybdenum oxide, iridium oxide, nickel oxide, and tantalum oxide.

33. A film comprising one or more metal oxides and an accelerant.

34. The film of claim 33, wherein said metal oxide is selected from the group of tin oxide, germanium oxide, titanium oxide, aluminum oxide, zirconium oxide, zinc oxide, indium oxide, cadmium oxide, hafnium oxide, tungsten oxide, vanadium oxide, chromium oxide, molybdenum oxide, iridium oxide, nickel oxide, and tantalum oxide.

35. The film of claim 33, wherein said accelerant is selected from the group consisting of phosphites, borates, water, alkyl phosphine, arsine and borane derivatives, PH<sub>3</sub>, AsH<sub>3</sub>, B<sub>2</sub>H<sub>6</sub>, O<sub>2</sub>, N<sub>2</sub>O, NF<sub>3</sub>, NO<sub>2</sub> and CO<sub>2</sub>.

36. The film of claim 33, wherein said accelerant is triethylphosphite.

37. The film of claim 33, further comprising a silicon oxide.

38. The film of claim 33, wherein said film is amorphous.

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39. An article comprising a substrate and a film of  
claim 33 deposited thereon.

40. An article comprising a substrate and a film of  
claim 34 deposited thereon.

41. An article comprising a substrate and a film of  
claim 35 deposited thereon.

42. An article comprising a substrate and a film of  
claim 36 deposited thereon.

43. An article comprising a substrate and a film of  
claim 37 deposited thereon.

44. An article comprising a substrate and a film of  
claim 38 deposited thereon.

45. An article of claim 39, wherein the substrate is  
glass.

46. An article of claim 39, wherein the film has a  
refractive index which changes continuously.

47. An article of claim 39, wherein the film comprises a  
plurality of layers.

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48. An article of claim 47, wherein each layer contains  
a mixture of tin and silicon oxides.

49. An article of claim 48, wherein each layer contains  
a concentration of tin oxide and silicon oxide different from  
an adjacent layer.

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## ABSTRACT

A composition for coating glass by chemical-vapor deposition comprises a mixture of a tin oxide precursor monobutyltin trichloride, a silicon dioxide precursor tetraethylorthosilicate, and an accelerant such as triethyl phosphate; the composition is gaseous below 200° C., and permits coating glass having a temperature from 450° to 650° C. at deposition rates higher than 350 Å/sec. The layer of material deposited can be combined with other layers to produce an article with specific properties such as controlled emissivity, refractive index, abrasion resistance, or appearance.

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202-408-4000

PATENT  
Attorney Docket No. 1222.0034

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Reissue Application of: )  
David A. Russo et al. )  
Serial No.: 08/544,212 )  
(Original Patent 5,401,305 issued )  
March 28, 1995, Original Serial )  
No. 104,125 filed December 13, 1993 )  
Filed: October 17, 1995 )  
For: COATING COMPOSITION FOR GLASS )  
Owner of Record: Elf Atochem North )  
America, Inc. )

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

REQUEST FOR CERTIFIED ABSTRACT OF TITLE

Please prepare a certified abstract of title for U.S. Patent No. 5,401,305, issued March 28, 1995, for placing in the file of the reissue application identified above.

Title to this patent stands in the name of Elf Atochem North America, Inc. The title was recorded on December 20, 1993 in application Serial No. 08/104,125, filed December 13, 1993, at Reel No. 6806, Frame No. 0592. A true copy of the assignment accompanies this request.

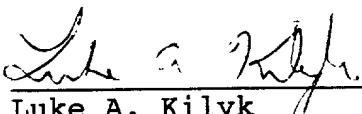
The owner Elf Atochem North America, Inc. is a corporation of the Commonwealth of Pennsylvania, with its principal offices at 2000 Market Street, Philadelphia, PA 19103-3222.

The fee required under 37 C.F.R. § 1.19(b)(4) is submitted herewith.

If there are any additional fees due in connection with the filing of this document, please charge the fees to our Deposit Account No. 06-0916. If a fee is required for an extension of time under 37 C.F.R. § 1.136 not accounted for above, such extension is requested and should also be charged to our Deposit Account.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER

By:   
Luke A. Kilyk  
Reg. No. 33,251

Date: January 11, 1996

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PATENT  
Attorney Docket No. 1222.0034

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Reissue Application of: )  
David A. Russo et al. )  
Serial No.: 08/544,212 )  
(Original Patent 5,401,305 issued )  
March 28, 1995, Original Serial )  
No. 104,125 filed December 13, 1993 )  
Filed: October 17, 1995 )  
For: COATING COMPOSITION FOR GLASS )  
Owner of Record: Elf Atochem North )  
America, Inc. )

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

OFFER TO SURRENDER

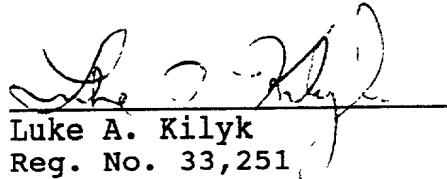
The undersigned attorney for the assignee of the accompanying reissue application for the reissue of Letters Patent No. 5,401,305 for COATING COMPOSITION FOR GLASS, issued on March 28, 1995, to David A. Russo, Ryan R. Dirkx, and Glenn P. Florczak, hereby offers to surrender the patent.

An order for a title report as required in reissue applications was filed on October 17, 1995.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER

By:

  
Luke A. Kilyk  
Reg. No. 33,251

Date: January 11, 1996

PATENT  
Attorney Docket No. 01222.0034

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Reissue Application of:    )  
  )  
David A. Russo et al.    )  
  )  
Serial No.: 08/544,212    )  
  )  
Filed: October 17, 1995    )  
  )  
For: COATING COMPOSITION FOR GLASS                                      )  
  )  
Owner of Record: Elf Atochem North                                      )  
  )  
  )

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

ASSENT OF ASSIGNEE TO REISSUE

Elf Atochem North America, Inc., the assignee of the  
above-identified U.S. patent, expressly authorizes the reissue of  
its U.S. Patent No. 5,401,305.

Date: Jan. 5, 1996

Elizabeth R. McIlwraith, Assistant  
Name and Title of Authorized Secretary  
Person Signing on Behalf of  
Elf Atochem North America, Inc.

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PATENT

Attorney Docket No. 1222.0034

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Reissue Application of: )  
David A. Russo et al. )  
Serial No.: 08/644,212 )  
(Original Patent 5,401,305 issued )  
March 28, 1995, Original Serial )  
No. 104,125 filed December 13, 1993 )  
Filed: October 17, 1995 )  
For: COATING COMPOSITION FOR GLASS )  
Owner of Record: Elf Atochem North )  
America, Inc. )

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

REISSUE DECLARATION UNDER 37 C.F.R. § 1.175

We, David A. Russo, Ryan R. Dirkx, and Glenn P. Florczak, the named inventors of the above-identified patent, declare and state as follows:

1. We are the named inventors of U.S. Patent No. 5,401,305 issued March 28, 1995, ("the '305 patent") which relates to a gaseous composition.

2. During the Summer of 1995, we were initially informed that the claims in the '305 patent did not claim the entire scope of our invention. In other words, we have been informed and agree that the '305 patent is partially inoperative because the claims in the '305 patent claim less than what is disclosed in the specification thereof.

3. In particular, the claims of the '305 patent relate to a gaseous composition adapted to deposit at least a first layer of tin oxide and silicon oxide onto glass at a rate of deposition greater than about 350 Å/seconds. However, the specification of the '305 patent, as well as the specification of the application leading to the '305 patent, disclose a broader gaseous composition. As reflected in the claims attached as Exhibit 1 to this declaration, we believe we are entitled to a broader invention which relates to a gaseous mixture comprising at least one metal oxide precursor and an accelerant, a film comprising at least one metal oxide and an accelerant, and a layer comprising a mixture of at least one metal oxide and an accelerant deposited on a substrate. The subject matter of these claims was not truly pursued in the prosecution of the application leading to the '305 patent and we believe this was based on a misunderstanding or error of the patent counsel for the assignee.

4. This misunderstanding or error, to the best of our knowledge, arose without any deceptive intention on our part, and unfortunately, was not recognized by us until pointed out by patent counsel, namely, Stanley A. Marcus.

5. We acknowledge our duty to disclose to the U.S. Patent and Trademark Office all information known to us which may be material to the patentability of the '305 patent and the new claims attached as Exhibit 1 to this Declaration.

6. We have reviewed and understand the contents of the original and reissue specifications, including the claims, as

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amended by any amendment, including the amendment attached to this Declaration.

7. We believe we are the inventors to the original '305 patent, as well as the claims set forth in the amendment attached to this Declaration for which a reissue patent is sought.

8. The newly presented claims differ from those of the original patent in that the claims of the '305 patent only relate to a gaseous composition comprising a precursor of tin oxide, a precursor of silicon oxide of formula  $R_mO_nSi_p$  and an accelerant selected from the group consisting of organic phosphites, organic borates, and water, and mixtures thereof, and a source of oxygen. The original patent claims do not specifically mention a mixture comprising at least one metal oxide and an accelerant, a coated layer comprising the mixture containing the at least one metal oxide and an accelerant, nor do they relate to a gaseous composition comprising at least one precursor of a metal oxide with an accelerant, as was specifically disclosed in the specification of the '305 patent, for instance, at column 4, lines 18-39, column 5, lines 20-45, column 5, lines 58-66, as well as the examples.

9. We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may

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jeopardize the validity of the application or any patent issued thereon.

Date: 1/5/96

David A. Russo  
David A. Russo

Date: 1/5/96

Ryan R. Dirkx  
Ryan R. Dirkx

Date: 1/5/96

Glen P. Florczak  
Glen P. Florczak

DO NOT FILE UNTIL 6 MONTHS AFTER FILING DATE

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28. A gaseous composition comprising at least one precursor of a metal oxide and an accelerant selected from the group consisting of organic phosphites, organic borates, and water.

29. The gaseous composition of claim 28, wherein at least one precursor for a metal oxide is selected from the group consisting of compounds of tin, germanium, titanium, aluminum, zirconium, zinc, indium, cadmium, hafnium, tungsten, vanadium, chromium, molybdenum, iridium, nickel, and tantalum.

30. The gaseous composition of claim 28, further comprising a precursor for a silicon oxide.

31. A gaseous composition comprising a metal oxide precursor and an accelerant selected from the group consisting of phosphites, borates, water, alkyl phosphine, arsine and borane derivatives,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{B}_2\text{H}_6$ ,  $\text{O}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NF}_3$ ,  $\text{NO}_2$  and  $\text{CO}_2$ .

32. The gaseous composition of claim 31, wherein the metal oxide precursor is a precursor of metal oxides selected from the group consisting of tin oxide, germanium oxide, titanium oxide, aluminum oxide, zirconium oxide, zinc oxide, indium oxide, cadmium oxide, hafnium oxide, tungsten oxide,

vanadium oxide, chromium oxide, molybdenum oxide, iridium oxide, nickel oxide, and tantalum oxide.

33. A film comprising one or more metal oxides and an accelerant.

34. The film of claim 33, wherein said metal oxide is selected from the group of tin oxide, germanium oxide, titanium oxide, aluminum oxide, zirconium oxide, zinc oxide, indium oxide, cadmium oxide, hafnium oxide, tungsten oxide, vanadium oxide, chromium oxide, molybdenum oxide, iridium oxide, nickel oxide, and tantalum oxide.

35. The film of claim 33, wherein said accelerant is selected from the group consisting of phosphites, borates, water, alkyl phosphine, arsine and borane derivatives,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{B}_2\text{H}_6$ ,  $\text{O}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NF}_3$ ,  $\text{NO}_2$  and  $\text{CO}_2$ .

36. The film of claim 33, wherein said accelerant is triethylphosphite.

37. The film of claim 33, further comprising a silicon oxide.

38. The film of claim 33, wherein said film is amorphous.

39. An article comprising a substrate and a film of claim 33 deposited thereon.

40. An article comprising a substrate and a film of claim 34 deposited thereon.

41. An article comprising a substrate and a film of claim 35 deposited thereon.

42. An article comprising a substrate and a film of claim 36 deposited thereon.

43. An article comprising a substrate and a film of claim 37 deposited thereon.

44. An article comprising a substrate and a film of claim 38 deposited thereon.

45. An article of claim 39, wherein the substrate is glass.

46. An article of claim 39, wherein the film has a refractive index which changes continuously.

47. An article of claim 39, wherein the film comprises a plurality of layers.

48. An article of claim 47, wherein each layer contains a mixture of tin and silicon oxides.

49. An article of claim 48, wherein each layer contains a concentration of tin oxide and silicon oxide different from an adjacent layer.

## DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: COATING COMPOSITION FOR GLASS the specification of which [ ] is attached and/or [X] was filed as United States Application Serial No. 08/544,212 on June 7, 1995 and was amended on \_\_\_\_\_ (if applicable); or was filed as PCT International Application Number \_\_\_\_\_ on \_\_\_\_\_ and was amended on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

COUNTRY (if PCT indicate PCT)	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
			[ ] Yes [ ] No

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

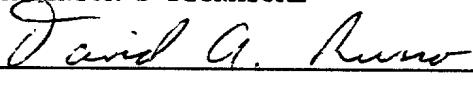
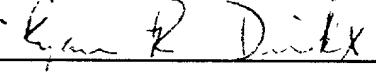
U.S. APPLICATIONS		STATUS (Check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED

PCT APPLICATIONS DESIGNATING THE U.S.		
PCT APPLICATION NO	PCT FILING DATE	U.S. SERIAL NUMBER ASSIGNED (if any)

I hereby appoint the following attorney and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, Reg. No. 22,540, Douglas B. Henderson, Reg. No. 20,291; Ford F. Farabow, Jr., Reg. No. 20,630; Arthur S. Garrett, Reg. No. 20,338; Donald R. Dunner, Reg. No. 19,073; Brian G. Brunsvoold, Reg. No. 22,593; Tipton D. Jennings, IV, Reg. No. 20,645; Jerry D. Voight, Reg. No. 23,020; Laurence R. Hefter, Reg. No. 20,827; Kenneth E. Payne, Reg. No. 23,098; Herbert H. Mintz, Reg. No. 26,691; C. Larry O'Rourke, Reg. No. 26,014; Albert J. Santorelli, Reg. No. 22,610; Michael C. Elmer, Reg. No. 25,857; Richard H. Smith, Reg. No. 20,609; Stephen L. Peterson, Reg. No. 26,325; John M. Romary, Reg. No. 26,331; Bruce C. Zotter, Reg. No. 27,680; Dennis P. O'Reilley, Reg. No. 27,932; Allen M. Sokal, Reg. No. 26,695; Robert D. Bajefsky, Reg. No. 25,387; Richard L. Stroup, Reg. No. 28,478; David W. Hill, Reg. No. 28,220; Thomas L. Irving, Reg. No. 28,619; Charles E. Lipsey, Reg. No. 28,165; Thomas W. Winland, Reg. No. 27,605; Basil J. Lewris, Reg. No. 28,818; Martin I. Fuchs, Reg. No. 28,508; E. Robert Yoches, Reg. No. 30,120; Barry W. Graham, Reg. No. 29,924; Susan Haberman Griffen, Reg. No. 30,907; Richard B. Racine, Reg. No. 30,415; Thomas H. Jenkins, Reg. No. 30,857; Robert E. Converse, Jr., Reg. No. 27,432; Clair X. Mullen, Jr., Reg. No. 20,348; Christopher P. Foley, Reg. No. 31,354; John C. Paul, Reg. No. 30,413; Roger D. Taylor, Reg. No. 28,992; David M. Kelly, Reg. No. 30,953; Kenneth J. Meyers, Reg. No. 25,146; Carol P. Einaudi, Reg. No. 32,220; Walter Y. Boyd, Jr., Reg. No. 31,738; Steven M. Anzalone, Reg. No. 32,095; Jean B. Fordis, Reg. No. 32,984; Barbara C. McCurdy, Reg. No. 32,120; James K. Hammond, Reg. No. 31,964; Richard V. Burgujian, Reg. No. 31,744; J. Michael Jakes, Reg. No. 32,824; and Stanley A. Marcus, Reg. No. 24,425; William D. Mitchell, Reg. No. 20,977; Robert G. Hoffmann, Reg. No. 17,767; and Royal E. Bright, Reg. No. 26,845. Please address all correspondence to FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER 1300 I Street, N.W., Washington, D.C. 20005, Telephone No. (202) 408-4000.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

FULL NAME OF FIRST INVENTOR <u>David A. RUSSO</u>	INVENTOR'S SIGNATURE 	DATE <u>1/5/96</u>
RESIDENCE <u>Norristown, Pennsylvania 19403</u>	COUNTRY OF CITIZENSHIP <u>United States</u>	
POST OFFICE ADDRESS <u>22 Brenda Lane</u> <u>Norristown, Pennsylvania 19404</u>		
FULL NAME OF SECOND INVENTOR <u>Ryan R. DIRKX</u>	INVENTOR'S SIGNATURE 	DATE <u>1/5/96</u>
RESIDENCE <u>Glenmoore, Pennsylvania 19343</u>	COUNTRY OF CITIZENSHIP <u>United States</u>	
POST OFFICE ADDRESS <u>2006 Turnberry Circle</u> <u>Glenmoore, Pennsylvania 19343</u>		

FULL NAME OF THIRD INVENTOR <u>Glenn P. FLORCZAK</u>	INVENTOR'S SIGNATURE <i>Glenn P. Florczak</i>	DATE 1/15/96
RESIDENCE East Brunswick, New Jersey 08816	COUNTRY OF CITIZENSHIP United States	
POST OFFICE ADDRESS 2 Hilltop Boulevard East Brunswick, New Jersey 08816		

PATENT  
Attorney Docket No. 1222.0034

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Reissue Application of: )  
David A. Russo et al. )  
Serial No.: 08/544,212 )  
(Original Patent 5,401,305 issued )  
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Filed: October 17, 1995 )  
For: COATING COMPOSITION FOR GLASS )  
Owner of Record: Elf Atochem North )  
America, Inc. )

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

DECLARATION OF STANLEY A. MARCUS

I, Stanley A. Marcus, declare and state as follows:

1. I am Patent Counsel for the assignee of the above-identified patent and reissue application, Elf Atochem North America, Inc., and was one of the attorneys appointed by David A. Russo, Ryan R. Dirkx, and Glen P. Florczak to prosecute the application leading to Patent No. 5,401,305 ("the '305 patent").

2. During the Summer of 1995, I was comparing the claims of the '305 with another patent for interference purposes. I became aware that the claims of the '305 patent claimed less than Messrs. Russo, Dirkx, and Florczak had a right to claim as inventors. In my opinion, as a result, the '305 patent is partially inoperative through this error.

3. This misunderstanding regarding the scope of the Russo et al. invention (i.e., the error) arose when I had a meeting with Atochem's Research and Development people to discuss the claims of the '305 patent as issued. Upon this review, I discovered that the claims claimed less of the invention as disclosed in the specification of the '305 patent. In particular, the claims of the '305 patent relate to a gaseous composition adapted to deposit at least a first layer of tin oxide and silicon oxide onto glass at a rate of deposition greater than about 350 Å/seconds, wherein the composition comprises a precursor of tin oxide, a precursor of silicon oxide or formula  $R_mO_nSi_p$ , an accelerant selected from the group consisting of organic phosphites, organic borates, and water and mixtures thereof, and a source of oxygen. The claims as presented in the amendment attached to the Russo et al. Declaration are different in that they relate to a gaseous mixture comprising at least one metal oxide precursor and an accelerant, a film comprising at least one metal oxide and an accelerant, and also relate to a layer comprising at least one metal oxide and an accelerant deposited on a substrate.

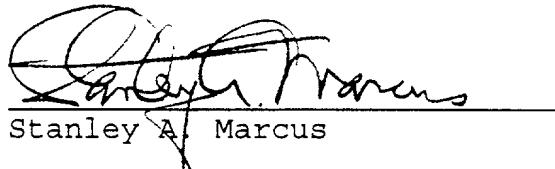
4. The misunderstanding or error arising from the scope of Russo et al.'s invention occurred without any deceptive intention on the part of the applicant, assignee, or applicant's counsel.

5. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false

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statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: January 5, 1996

  
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**Certificate Under 37 CFR 3.73(b)**

Applicants: David A. Russo, Ryan R. Dirkx, and Glen P. Florczak

Patent No.: 5,401,305 Issued: August 13, 1991

For: Coating Composition for Glass

Elf Atochem North America, Inc., a Corporation

(Name of Assignee) (Type of Assignee, e.g., corporation,  
partnership, university, government  
agency, etc.)

certifies that it is the assignee of the entire right, title and interest in  
the patent identified above by virtue of either:

A. [X] An assignment from the inventor(s) of the patent identified above. The  
assignment was recorded in the Patent and Trademark Office at Reel 6806,  
Frame 0592, or for which a copy thereof is attached.

OR

B. [ ] A chain of title from the inventor(s), of the patent identified above, to  
the current assignee as shown below:

1. From: \_\_\_\_\_ To: \_\_\_\_\_

The document was recorded in the Patent and Trademark Office  
at Reel \_\_\_\_, Frame \_\_\_\_, or for which a copy thereof is  
attached.

2. From: \_\_\_\_\_ To: \_\_\_\_\_

The document was recorded in the Patent and Trademark Office  
at Reel \_\_\_\_, Frame \_\_\_\_, or for which a copy thereof is  
attached.

3. From: \_\_\_\_\_ To: \_\_\_\_\_

The document was recorded in the Patent and Trademark Office  
at Reel \_\_\_\_, Frame \_\_\_\_, or for which a copy thereof is  
attached.

[ ] Additional documents in the chain of title are listed on a  
supplemental sheet.

[ ] Copies of assignments of other documents in the chain of title are  
attached.

The undersigned has reviewed all the documents in the chain of title of the patent identified above and, to the best of undersigned's knowledge and belief, title is in the assignee identified above.

The undersigned (whose title is supplied below) is empowered to sign this certificate on behalf of the assignee.

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: January 5, 1994

Name: Elizabeth L. McDermott

Title: Assistant Secretary

Signature: Elizabeth L. McDermott